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Models of Rhodium Complexes Bound to Silica: Preparation, Structure, and Interconversion of Dinuclear (Silyloxy)rhodium Complexes

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The "two-dimensional chemistry"[1] of supported metal complexes and oxide type supports represents one of the most active challenges[2] of transition metal catalysis.

The outstanding catalytic activity of rhodium attracted considerable attention to the surface chemistry of this metal.[3] It has been established[4] that rhodium carbonyls easily undergo reductive clusterification/oxidative declusterification reaction sequences on the surface of oxide supports (e.g. SiO_2, Al_2O_3, MgO, TiO_2, etc.), but the structure of the surface species involved in these reactions is not yet fully explored.

Our groups made early efforts at preparing molecular models[5,6] of these species. Now we report the synthesis and structure of dinuclear rhodium silanolate complexes where the metals are in an olefinic or carbonyl coordination environment.

Experimental Section

All operations[7] were carried out under a carefully dried, deoxygenerated, and CO_2-free Ar or CO atmosphere. Dried, deoxygenated solvents were used.

Infrared spectra were recorded on IR-75 (Carl Zeiss, Jana, Germany) and Bruker FT-IR IFS 113 V instruments. ^{1}H-NMR spectra were obtained with a Bruker WP 80 SY (FT, 80 MHz) spectrometer. X-ray diffraction experiments were performed using an Enraf-Nonius CAD-4 diffractometer.

Starting materials were of commercial origin, except for $Cl_2Rh_2(CO)_4$,[8] $Cl_2Rh_2(COD)_2$,[9] $(OH)_2Rh_2(COD)_2$[10] (from commercial $RhCl_3 \cdot xH_2O$), Me_3SiONa, Et_3SiONa, and Ph_3SiONa, which were prepared according to published procedures.[11] We found that careful preparation of the sodium silanolates was very critical.

Examples of the preparative methods are given below; additional derivatives were prepared analogously.

Preparation of $(R_3SiO)_2Rh_2(COD)_2$ (2) Complexes. Method A (by Ion Metathesis) (R = Ph) (Reaction i). $Cl_2Rh_2(COD)_2$, 100 mg (0.20 mmol), was dissolved in 50 mL of dry *n*-pentane under Ar atmosphere at room temperature, in a Schlenk vessel. To this stirring solution was added at once Ph_3SiONa, 66 mg (0.22 mmol). The reaction was followed by ^{1}H-NMR spectroscopy, with samples taken every 15 min. After 60−90 min a new band system (later proved belonging to **2** (R = Ph)) became dominant. Then the solution was concentrated to $^1/_2$ volume and filtered, and the filtrate was left to stand on dry ice for 1−3 nights. A white crystalline precipitate was obtained, which was filtered off while cold. The crude product was recrystallized from *n*-pentane at −10 °C. Yield (crude product): 140−175 mg (70−90%). Yield (crystalline product): 39−97 mg (20−50%).

Method B (by Silylation) (R = Me) (Reaction ii). $(HO)_2Rh_2(COD)_2$, 50 mg (0.11 mmol), was dissolved in 30 mL of *n*-pentane under Ar atmosphere at room temperature. To this stirring solution was added at once BSTFA (*N,O*-bis(trimethylsilyl)trifluoroacetamide), 62 mg (60 μL, 0.24 mmol). The solution was stirred at room temperature for 2−3 h. Then a sample was analyzed by ^{1}H-NMR spectroscopy: resonances of the starting material disappeared and a new band pattern dominated, which was later attributed to $(Me_3SiO)_2Rh_2(CO)_2$. The solution was next concentrated to $^1/_3$ of its volume. The residual solution was then chilled to −18 °C for 1 night and then to −78 °C for an additional 1 night. A white powder separated, which was recrystallized from Et_2O/*n*-pentane (1:9); the product (87 mg, 66%) was identified as $(Me_3SiO)_2Rh_2(COD)_2$.

Method C (by Terminal Ligand Exchange) (R = Me) (Reaction iv). $(Me_3SiO)_2Rh_2(CO)_4$, 43 mg (0.05 mmol), was dissolved in 10 mL of *n*-pentane, under Ar atmosphere at room temperature. To this stirring solution was added *cis,cis*-1,5-cyclooctadiene, 33 mg (29 μL, 0.3 mmol). The solution was stirred for 1 h at room temperature and analyzed by IR spectroscopy, which showed that the ν(C−O) bands of **4** (R = Ph) had disappeared. Then the solvent was evaporated, the residue was extracted by 2 mL of $CDCl_3$, and this solution was analyzed by ^{1}H-NMR spectroscopy. Quantitative conversion of **4** (R = Ph) into **2** (R = Ph) was observed. The product was not isolated.

Preparation of $(R_3SiO)_2Rh_2(CO)_4$ (4) Complexes. Method A (by Terminal Ligand Exchange) (R = Ph) (Reaction iii). $(Ph_3SiO)_2Rh_2(COD)_2$, 50 mg (0.051 mmol), was dissolved in 30 mL of *n*-hexane under Ar atmosphere. Then the atmosphere over this solution was gradually changed to Ar/CO (~1:1) while the solution was stirred. After 10 min a sample was analyzed by IR spectroscopy in the 2200−1600 cm^{-1} range. The band system characteristic for $X_2Rh_2(CO)_4$ complexes[12] appeared (see below). After an additional period of 20 min

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Table 1. Characterization of the Complexes $(\mu_2\text{-}R_3SiO)_2Rh_2L_4$

complex		anal. (%)						
L_4	R	atom	found	calcd	formula	^{1}H-NMR (δ, ppm; vs TMS)	IR (cm^{-1})	X-ray
$(COD)_2$ (**2**)	Me	C	44.2	44.00	$C_{22}H_{42}O_2Rh_2Si_2$	CD_2Cl_2: 0.13 (virtual t, splitting 0.04 ppm, 18H, SiC*H*$_3$); 1.95 (s, br, 8H, allyl-*H*); 2.60 (s, br, ~3 components, 8H, allyl-*H*); 4.10 (s, br, 8H, C*H*)	KBr pellet: 1480, ν(C=C); 1175 (t), ν(Si−C(Me)); 810, ν(Si−O)	−
		H	7.3	7.05				
	Ph	C	64.5	64.19	$C_{52}H_{54}O_2Rh_2Si_2$	$CDCl_3$: 1.66 and 2.43 (m, 16 H, C*H*$_2$); 3.51 (s, br, 8H, C*H*); 7.25−7.75 (m, 30H, C_6*H*$_5$)	KBr pellet: 1479, ν(C=C); 1109, ν(Si−C(Ph)); 920, ν(Si−O)	+
		H	5.9	5.59				
		Rh	21.1	21.15				
$(CO)_4$ (**4**)	Me						*n*-hexane, ν(C−O): 2088.0 m, 2072.0 s, 2059.9 w (^{13}C−O), 2009.2 s, 1977.1 w (^{13}C−O)	−
	Et						*n*-hexane, ν(C−O): 2087.5 m, 2075.0 vs, 2064.0 w (^{13}C−O), 2012.5 s, 1981.5 w (^{13}C−O)	−
	Ph	C	55.5	55.31	$C_{40}H_{30}O_6Rh_2Si_2$	C_6D_6: 7.3−7.8 (m, 30H, C_6*H*$_5$)	*n*-hexane, ν(C−O): 2094.4 m, 2076.1 s, 2064.6 w (^{13}C−O), 2014.0 s, 1982.9 w (^{13}C−O)	+
		H	3.7	3.48				
		Rh	23.6	23.69				

Table 2. Crystallographic Data for $(\mu_2\text{-}Ph_3SiO)_2Rh_2(1,5\text{-cyclooctadiene})_2$ (**2**) and $(\mu_2\text{-}Ph_3SiO)_2(CO)_4$ (**4**)

chem formula	$C_{52}H_{54}O_2Rh_2Si_2$	$C_{40}H_{30}O_6Rh_2Si_2$
fw	972.99	868.66
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a, Å	10.727(3)	9.578(2)
b, Å	12.867(2)	15.657(2)
c, Å	16.161(2)	24.565(4)
α, deg	89.05(1)	
β, deg	86.41(2)	91.41(2)
γ, deg	84.66(2)	
V, Å^3	2216(1)	3683(2)
Z	2	4
D_x, g cm^{-3}	1.46	1.57
T, K	295(2)	295(2)
μ(Mo Kα), cm^{-1}	8.24	9.90
$R(F)^a$	0.035	0.030
$R_w(F)^b$	0.034	0.031

^{a} $R = \sum||F_o| - |F_c||/|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

however the characteristic ν(C−O) bands[13] of $Rh_4(CO)_{12}$ started to appear. Then the atmosphere over the solution was changed to Ar, $^2/_3$ of the solvent was evaporated, and the solution was chilled at −78 °C overnight. A yellowish white solid product was obtained, which was recrystallized from *n*-pentane and identified as $(Ph_3SiO)_2Rh_2(CO)_4$. Yield (pure product): 21 mg, 47%. This and similar reactions under nondiluted CO atmosphere resulted in a quick color change from yellowish to deep red, indicating the easy formation of $Rh_4(CO)_{12}$ (confirmed also by IR spectroscopy).

Method B (by Ion Metathesis) (R = Ph) (Reaction v). Essentially the method published in ref 5a,c was used. Yield (R = Ph) of the crude product ranged 30−70%, while the (analytically pure) crystalline products could be isolated only in yields of 5−20%.

Characterization of the Products. The products were characterized by elemental analysis, ^{1}H-NMR and IR spectroscopy, and X-ray diffraction. The results are collected in Table 1.

Crystal Structure Determinations. Crystallographic data are collected in Table 2. Intensities were measured on a CAD4 automatic diffractometer (Mo Kα radiation, λ = 0.710 73 Å) at room temperature with θ ranging from 3 to 25°. Data were corrected from absorption (maximum and minimum relative transmission factors 1.00−0.96 and 1.00−0.95 for **2** and **4**, respectively) and Lorentz−polarization effects. The structure were solved by Patterson methods and refined by full-matrix least squares using the SDP-Plus structure determination package. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. Hydrogen atoms were introduced in the final stages of refinement in calculated positions (d_{C-H} = 0.95 Å) with a common overall thermal factor.

Results and Discussion

The preparative results are summarized in Scheme 1. It was observed that the dimeric silanolate−rhodium 1,5-cyclooctadiene (COD), complexes are formed smoothly and almost quantitatively from the corresponding chloro derivative **1** by ion metathesis (reaction i).

An alternative way for obtaining complex **2** (R = Me) was found by silylation (with the conventional organic derivatizing agent BSTFA) of the coordinated OH groups in $(\mu_2\text{-}OH)_2Rh_2(COD)_2$ (**3**) (reaction ii). It should be mentioned that complex **3** is also a model of interaction of Rh with (more basic) oxide surfaces and the reaction of its OH groups hints at a considerable mobility of the coordinated hydroxyl proton. The "functionalization" of coordinated OH groups finds only a few precedents.[14]

Complex **2** can smoothly be carbonylated[15] into the corresponding tetracarbonyl compound (**4**) if **2** is exposed to diluted CO atmosphere for a few minutes (reaction iii). More concentrated CO or longer reaction time leads quickly to quantitative transformation of all Rh into $Rh_4(CO)_{12}$ (reductive clusterification). This latter reaction appears to be a general feature of rhodium complexes with oxygen ligands.[4d,5a,c] The carbonylation can be reversed by excess COD (under Ar) (reaction iv).

Complexes **4** can be obtained alternatively[5c] by ion metathesis from $Cl_2Rh_2(CO)_4$ (**5**).

Complexes **2** and **4** were characterized by elemental analyses and spectroscopic methods. The crystal and molecular structures of representatives of both types were determined by X-ray

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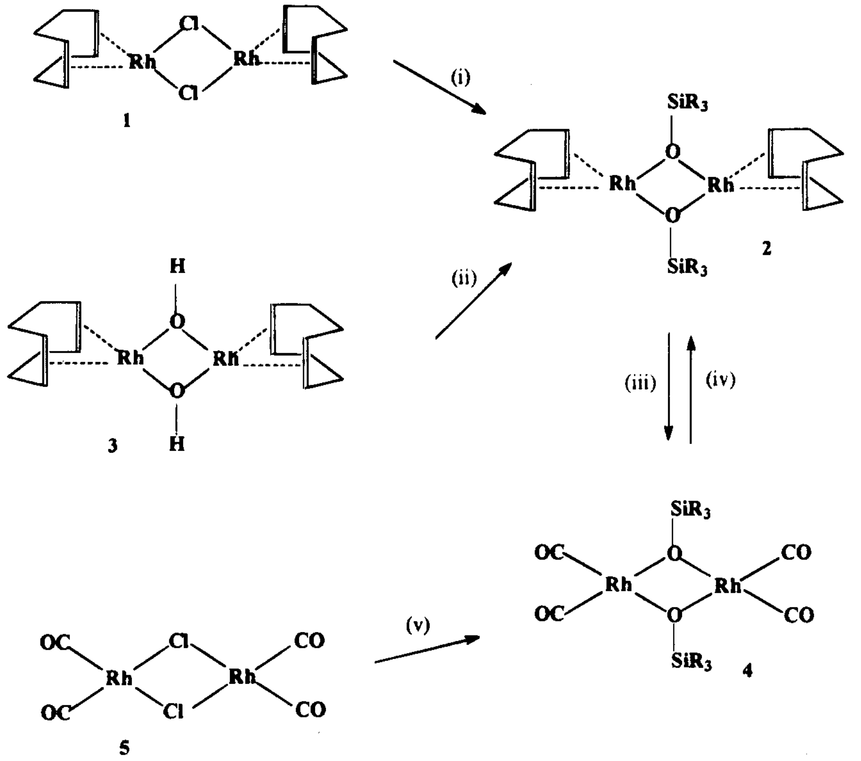
Scheme 1[a]



[a] Reagents and conditions: (i) R_3SiONa, *n*-hexane, 25 °C, Ar, 180 min (R = Me, Ph); (ii) *N,N*-bis(trimethylsilyl)trifluoroacetamide (BSTFA), *n*-hexane, 25 °C, Ar, 30 min (R = Me); (iii) *n*-hexane, 25 °C Ar/CO (1:1), 20−30 min (R = Ph); (iv) 1,5-cyclooctadiene (COD) 3−5-fold excess, *n*-hexane, 25 °C, Ar, (R = Ph); (v) R_3SiONa, *n*-pentane, 25 °C, Ar, 30−50 min (R = Me, Et, Ph).

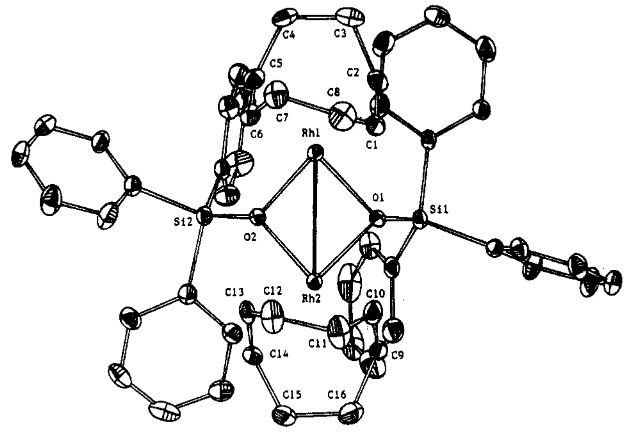


Figure 1. ORTEP drawing of $(\mu_2\text{-}Ph_3SiO)_2Rh_2(COD)_2$ (**2**, R = Ph). For sake of clarity H atoms have been omitted. Significant bond lengths (Å) are as follows: Rh−Rh, 2.785(1); Rh−O(av), 2.116; O−Si(av), 1.630; Si−C(Ph)(av), 1.873; Rh−$C(sp^2)$(av), 2.101; $C(sp^2)$−$C(sp^2)$-(COD)(av), 1.383. Angles (deg) are as follows: Rh−O−Rh(av), 82.3; Rh−O−Si(av), 136.1; O−Rh−O(av), 79.1; O−Si−C(Ph)(av), 111.2; ω, 109.6.

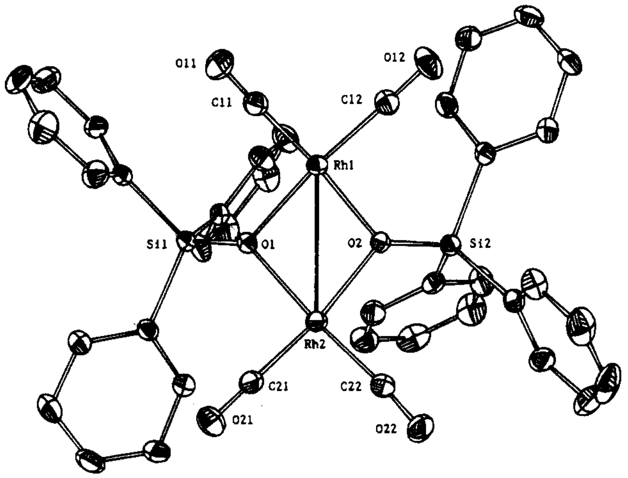


Figure 2. ORTEP drawing of $(\mu_2\text{-}Ph_3SiO)_2Rh_2(CO)_4$ (**4**, R = Ph). For sake of clarity H atoms have been omitted. Significant bond lengths (Å) are as follows: Rh−Rh, 2.922(1); Rh−O(av), 2.062; O−Si(av), 1.637; Si−C(Ph)(av), 1.869; Rh−C(O)(av), 1.828; C−O(av), 1.130. Angles (deg) are as follows: Rh−O−Rh(av), 90.2; Rh−O−Si(av), 133.2; O−Rh−O(av), 77.5; O−Si−C(Ph)(av), 109.6; ω, 126.5.

diffraction (Figures 1 and 2). Complexes **2** (R = Ph) and **4** (R = Ph) are the first structurally characterized compounds with a Si−O−Rh bond sequence. Both molecules show relatively short intramolecular metal−metal distances,[15,16] which can be considered indicative of some Rh−Rh bonding interactions. Nevertheless, the great shortening of the Rh−Rh distances on moving from the μ-Cl to the μ-$OSiPh_3$ derivatives, i.e. 3.12 vs 2.92 Å for $[(\mu\text{-}X)Rh(CO)_2]_2$ and 3.50 vs 2.78 Å for $[(\mu\text{-}X)Rh(COD)]_2$ (X = Cl,[6a,b] $OSiPh_3$) is representative more of the dimensions of the bridging atoms (and, *vide infra*, of the different packing forces affecting the value of the roof angle) rather than of the strengths of the Rh−Rh interactions.

Complexes **2** and **4** have a roof-shaped bis-square planar overall geometry, and it seems likely that the electronic forces responsible for the bending around the X···X hinge (X = O, Cl) are comparable in magnitude to packing forces. In fact, the roof angle of $[(\mu\text{-}Ph_3SiO)Rh(COD)]_2$ (109.6°) is smaller (and the Rh−Rh distance shorter) than that of $[(\mu\text{-}Ph_3SiO)Rh(CO)_2]_2$ (126.5°); on the contrary, the μ-Cl derivative possessing the

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larger roof angle (and the shorter Rh—Rh distance) is the *planar* $[(\mu\text{-Cl})Rh(COD)]_2$.

These effects of the bridging ligands (X) on the geometry of the $[(\mu\text{-X})RhL_2]_2$ type complexes can be also discussed in terms of repulsive interactions between filled (p) orbitals of X and (d) of Rh.[17,18]

The $\mu\text{-OSiPh}_3$ derivatives have intermolecular Rh••Rh distances larger than 4.0 Å; this may be in accordance with their pale color.

The observations on compounds **2** and **4** reported here support the possibility of the formation of dinuclear rhodium surface complexes on silica[3a,b,h,i] (and perhaps on other oxides). The easy interconversion and clusterification reactions observed indicate that the formulation of the actual surface species requires the greatest care, since nuclearity, ligands, and oxidation number of surface rhodium complexes appear to depend very sensitively on the actual reaction conditions.

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Supplementary Material Available: Text describing the X-ray procedures and tables listing detailed experimental data for X-ray diffraction, fractional atomic coordinates, anisotropic thermal parameters, and bond distances and angles (20 pages). Ordering information is given on any current masthead page.

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(17) This aspect was pointed out by one of the reviewers of this paper. This important suggestion is gratefully acknowledged.

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